

Claims

5 1. A chromium(VI)-free, chromium(III)-containing and substantially coherent conversion layer on zinc or zinc alloys, **characterised in that**

10 even in the absence of further components such as silicate, cerium, aluminum and borate it presents a corrosion protection of approx. 100 to 1000 h in the salt spray test according to DIN 50021 SS or ASTM B 117-73 until first attack according to DIN 50961 Chapter 10;

15 it is clear, transparent and essentially colorless and presents multi-colored iridescence;

20 it has a layer thickness of approx. 100 nm to 1000 nm; and

25 it is hard, adheres well and is resistant to wiping.

2. A conversion layer according to claim 1, characterised in that it has across the conversion layer thickness a chromium content of up to approx. 1%, in relation to zinc and chromium in the conversion layer an average chromium content of more than approx. 5%;

30 it has a chromium-rich zone > approx. 20% chromium, in relation to zinc and chromium in the conversion layer, of more than approx. 15 nm; and

35 it has a chromium index > approx. 10.

3. A conversion layer according to claim 1 or 2, characterised in that it may contain, for further enhanced corrosion protection,

additional components selected from the group consisting of:
silicate, cerium, aluminum and borate;

5 additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr; Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

10 anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

15 polymers, in particular organic polymers, corrosion inhibitors; silicic acids, in particular colloidal or disperse silicic acids; surfactants; diols, triols, polyols; organic acids, in particular monocarboxylic acids; amines; plastics dispersions; dyes, pigments, in particular carbon black, chromogenic agents, in particular metallic chromogenic agents; amino acids, in particular glycine; siccatives, in particular cobalt siccatives; dispersing agents; and

20 mixtures thereof.

25

4. A conversion layer according to any one of claims 1 to 3, characterised in that it is a basis for further inorganic and/or organic layers.

30

5. A conversion layer according to any one of claims 1 to 4, characterised in that it contains dyes or color pigments for modification of the inherent color thereof.

35

6. A conversion layer according to any one of claims 1 to 5, characterised in that its layer thickness is approx. 100 nm.

7. A method for producing chromium(VI)-free conversion layers affording at least the corrosion protection of conventional chromium(VI)-containing yellow chromations, wherein

5 a metallic surface, in particular one of zinc or zinc alloys, in particular with iron, is treated with a solution of at least one chromium(III) complex and at least one salt;

10 **characterised in that**

the concentration of the chromium(III) complex is increased in comparison with a conventional trivalent blue chromation; and/or

15 a chromium(III) complex is used having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.

20 8. A method according to claim 7, characterised in that treatment is carried out at an elevated temperature, in particular 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.

25 9. A method according to any one of claims 7 or 8, characterised in that the ligands of the chromium(III) complex are selected from the group consisting of:

30 chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

35 furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and

further chelate ligands such as acetylacetone, urea, urea derivatives, and

5 further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur (-NR₂, -PR₂, wherein R independently is an organic, in particular aliphatic radical and/or H, and/or -SR, wherein R is an organic, in particular aliphatic radical or H); phosphinates and phosphinate derivatives; as well as

10 suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and H₂O and/or

15 the method is performed repeatedly on the surface to be passivated.

20

10. A concentrate for producing a passivation solution for surfaces of zinc or zinc alloys, in particular ones with iron, wherein it substantially contains chromium(III) for a passivating component,

characterised in that

25 the chromium(III) is present in the form of at least one complex having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.

30

11. A concentrate according to claim 10, characterised in that the chromium(III) complex is selected from complexes with chromium(III) and at least one ligand from the group consisting of:

35 chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

5 furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and

10 further chelate ligands such as acetylacetone, urea, urea derivaties, and

15 further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur (-NR₂, -PR₂, wherein R independently is an organic, in particular aliphatic radical and/or H, and/or -SR, wherein R is an organic, in particular aliphatic radical or H,); phosphinates and phosphinate derivatives; as well as

20 suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and H₂O.

25

12. A concentrate according to any one of claims 10 or 11, characterised in that the concentrate is present in solid or liquid form.

30

13. A concentrate according to any one of claims 10 to 12, characterised in that it contains further additives selected from the group consisting of: sealers, dewatering fluids; and

35 additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr; Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particuar sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

polymers, in particular organic polymers, corrosion inhibitors:
5 silicic acids, in particular colloidal or disperse silicic acids;
surfactants; diols, triols, polyols; organic acids, in particular
monocarboxylic acids; amines; plastics dispersions; dyes,
pigments, in particular carbon black, chromogenic agents, in
particular metallic chromogenic agents; amino acids, in
particular glycine; siccatives, in particular cobalt siccatives;
dispersing agents; as well as
10 mixtures thereof.

14. A passivation bath for passivating metal surfaces, in particular
ones of zinc, cadmium or aluminum, or alloys of these metals
15 among each other and/or with other metals, in particular with
iron,
characterised in that
20 it substantially contains chromium(III) as a passivating
component, wherein chromium(III) is present in a
concentration of approx. 5 to 100 g/l.

25 15. A passivation bath according to claim 14, characterised in that
chromium(III) is present in a concentration of approx. 5 g/l to
80 g/l, in particular of approx. 5 g/l to 60 g/l, in a particularly
preferred manner of approx. 10 g/l to 30 g/l, preferably
approx. 20 g/l.

30 16. A passivation bath according to claim 14 or 15, characterised
in that it has a pH between approx. 1.5 and 3.

35 17. A passivation bath according to any one of claims 14 to 16,
characterised in that it contains approx. 20 g/l chromium(III)
and has a pH of approx. 2 to 2.5.

18. A passivation bath according to any one of claims 14 to 17, characterised in that it contains further additives in particular selected from the group consisting of sealers, dewatering fluids; and

5 additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr; Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

10 anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

15 polymers, corrosion inhibitors; silicic acids, in particular colloidal or disperse silicic acids; surfactants; diols, triols, polyols; organic acids, in particular monocarboxylic acids; amines; plastics dispersions; dyes, pigments, in particular carbon black, chromogenic agents, in particular metallic chromogenic agents; amino acids, in particular glycine; siccatives, in particular cobalt siccative; dispersing agents; as

20 well as

25 mixtures thereof.

30 19. A passivation bath according to any one of claims 14 to 18, characterised in that it has a bath temperature of approx. 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.

35 20. A method for passivating surfaces of zinc or zinc alloys, in particular ones with iron,

characterised in that

the objects to be treated are immersed in a passivation bath according to any one of claims 14 to 19.

5

21. A method according to claim 20, characterised in that the immersion period is between approx. 15 and 200 seconds, in particular between approx. 15 and 100 seconds, preferably approx. 30 seconds.

10

22. A method according to any one of claims 20 or 21, characterised in that it is an elevated-temperature chromate coating method with rinsing water recycling over at least 2 cascaded rinsing stages.

15

23. A method according to claim 22, characterised in that a blue chromation is performed in one of the rinsing steps.

20

24. A passive layer obtainable by a method according to at least one of claims 20 to 23.

25

25. A passive layer according to claim 24, characterised in that it imparts a corrosion protection to an object such as to present a corrosion protection of at least 100 hours in the salt spray test according to DIN 50021 SS until first attack according to DIN 50961 Chapter 10.,

30

26. A passive layer according to claim 24 or 25, characterised in that it presents a greenish, red-green iridescent color for zinc.

35

27. A passive layer according to any one of claims 24 to 26, characterised in that its layer thickness is approx. 100 nm.

28. A conversion layer obtainable by a method according to at least one of claims 7 to 9.